

Analysis on Properties of Blend of PolyPropylene and Poly(ethylene-1-octene)

Huiying Wen, Shengling Xiao, Guiying Wang

*The Department of Packaging Engineering College of Engineering and Technology, Northeast Forestry University
Harbin 150040, PR China*

hywen80@yahoo.com.cn, shenglingxiao@yahoo.com.cn, cindy1996@yeah.net

Abstract: Polypropylene is a common used packaging material due to its many advantages, such as low price, light in weight, stable property and so on. But the notable flaw is its brittleness at low temperature. A Poly(ethylene-1-octene) copolymer is chosen as a blend to improve the processing properties of polypropylene. Studies on polymer process should be including not only the complicated structures for the various species but also the influence of external field such as shear on the polymer structures. In this work the crystallization morphology and structure of blend PP/PEcO is investigated through the LLS, TG, POM, WAXD and SR-SAXS techniques. For blend PP/PEcO, it is found that the morphology of sphere crystal obviously changes with the increasing amount of PEcO. Shear induces the orientation of crystallites and lamellae. The differences of shear effect between crystallite and lamellae may support the mesomorphic phase concept of flexible polymer crystallization.

Keywords: blend; SR-SAXS; lamellar; crystallite

1. Introduction

As a representative thermoplastic polymer, isotactic polypropylene absorbs much attention for its many good performance such as high mechanics behavior and processing characteristics[1]. But the drawback of brittleness and low compact intensity which seriously influence its use property. Polymer modifications have been carried out in many ways resulting in various properties depending on factors such as the blend composition, processing conditions, additives and the temperature of application. In practical processing, the product is supposed to be with low heat constriction coefficient which shows perfect size stability. For these purpose, more and more study is focus on the blend alloy[2-4]. The blend of iPP and metallocene catalyst elastomer poly(ethylene-co-octene) is a good example. Polymers produced by metallocene catalysts generally exhibit narrow molecular weight distribution and homogeneous comonomer distribution. These features make the new copolymers excellent for fundamental studies of structure property relationships of ethylene copolymers blended with other semicrystalline polymers[5-8]. Studies on polymer process should be including not only the complicated structures for the various species but also the influence of temperature, pressure and shear on the polymer structures. Although the blend shows obvious advantages during the processing, it is difficult to dispose if the complicated fundamental theory of polymer blend can not be understood. For example, the liquid-liquid phase separation and crystallization could be exist in blend at one time during the processing which result in complicated morphology and uncontrolled properties.

In this work the crystallization structure of obtained blend PP/PEcO is investigated through the TG, POM, DSC, WAXD and SR-SAXS techniques. The crystallization morphology and structure are reported and the theory of crystallization is discussed.

2. Experimental Section

2.1. Materials

The isotactic polypropylene homopolymer employed in this work is a commercial product of Aldrich Chemical Co., Inc. The Mw and Mn determined by gel permeation chromatography (GPC) are 339 869 and 74 492, respectively, and the iPP is used as received. Ethylene-octene copolymers is of the metallocene catalyst type with octene content 39% produced by Dow Chemicals Europe.

2.2. Sample Preparation and Characterizat

In this work the process of banburying is followed. The blend comprises iPP weight content 100%, 90%, 60% and 30% which are named as iPP100, iPP90, iPP 60 and iPP 30 respectively. The blend is heated to 200 °C and kept mixing until reaching steady state, afterwards, extruded to the room temperatre for further use. A Linkam CSS450 shear cell (U.K. Linkam Scientific Instruments, Ltd., Tadworth, Surrey) is used to control the temperature and shear rate. The sample is first melted and kept for a certain time to eliminate any residual effects, then cooled to crystallization temperature with a rate of -30 K /min. The thickness of the samples is adjusted to 1000 µm. The crystallization temperature is set to 140 °C. During this

(supported by No. RC2010XK002001)

process, a 5s step-shear with different shear rate is applied to the samples as soon as the isothermal crystallization temperature is reached. Then the sample is kept at the fixed temperature until complete crystallization and investigated by ex situ WAXD. The WAXD measurements are carried out at room temperature with a Rigaku D/max 2000V PC diffractometer with curved graphite crystal filtered Cu KR radiation source ($\lambda=0.154$ nm) at 40 kV and 200 mA. In situ rheoptical experiments are performed with a Leica DMR Polarizing microscope equipped with a JVC color video camera (TKC1381), Linkam Optical Shearing Stage (CSS 450) and laser light scattering spectrometer. Morphological changes during shear-induced crystallization are recorded by time-resolved optical measurements. Some blend samples are chosen for in-situ synchrotron SAXS observations. The samples are fixed by two capton tape covered steel slices for X-ray investigations.

3. Results and discussion

During the process of banburying one condition must be focused on which is decomposition temperature. Figure 1 shows TG datas of iPP and PEcO, one can see that the decomposition temperature are all higher than 200 °C. We choose 200 °C as the banburying temperature for the blends. Taking iPP90 as a example, the process of banburying can be depicted in Figure 2.

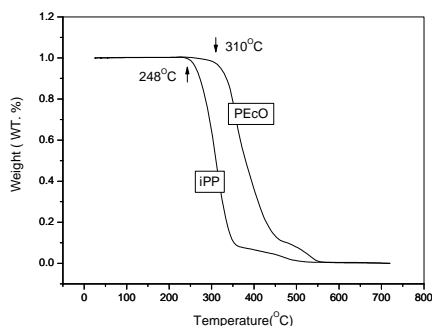


Figure 1. TG datas of iPP and PEcO.

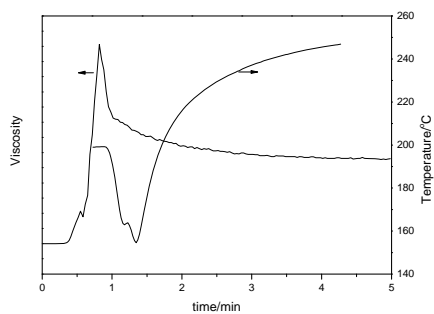


Figure 2. Banburying process for blend iPP90.

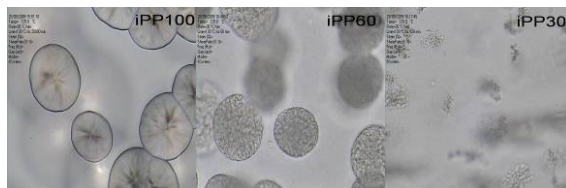


Figure 3. POM photos of iPP100, iPP60 and iPP30 during isothermal crystallization.

In blend iPP is a component with crystallization performance and PEcO is as a elaster which can not crystallite. To explore the phase structure, we observe the blend crystallization process by Polarizing Optical Microscope equipment. Fig 3 shows the polar photos for iPP100, iPP60 and iPP30 during crystallization. The boundary of pure iPP sphere crystal seems clear and the crystallization structure is very regular. With the elaster amount increasing, the crystallite morphology changes obviously which shows faint boundary and weak structural regularity. With the further enhancing content of PEcO(iPP30), the crystal morphology shows open-arms structure. We can see that the amount of PEcO in blend makes a notable influence on the crystal structure.

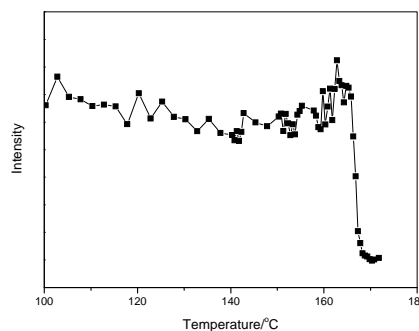


Figure 4. Variation of intensity from the laser light scattering patterns of iPP90 during the heating period at rate 10 K/min.

After complete crystallization, the samples are heated to melt state to explore the intensity varieties by the equipment of the laser light scattering. Let’s take iPP90 as a example, from figure 4 we can see that just before the blend melting there shows a very noticeable enhancement for scattering intensity. As is well known, the scattering intensity is dependent on the electron density difference between the phases of the system. Obviously some preordered structure exists in the initial crystallization stage which determines the intensity increasement during heating melt. Crystallization in polymer systems is a process which transfers the entangled macromolecules in the melt into a semi-crystalline state. Studying the melting is a reverse process which can give some clue to crystallite structure. Different from low molar mass compounds polymer systems never turn into perfect crys-

tals but end up in a metastable state which is crystalline in part. A semi-crystalline polymer is usually composed of lamellar crystallites which are separated by amorphous layers. Recently, many researcher found the earliest growing spherulites which can be detected already have sizes of nanometers size. It is noteworthy that this is far away from the initial stages of spherulite nucleation and growth. These early stages have recently gained particular importance in the discussion of the basic mechanism of polymer crystallization[9-11]. There are several experimental observations that lead to an assumption of crystal nucleation and growth which includes an intermediate phase, although a commonly accepted view is not yet evolved. Some authors propose a preceding coverage of the whole volume by a mesomorphic phase which develops by a mechanism resembling a spinodal process while others point at indication of nucleation for mesomorphic phase formation. In this paper, we show the results providing evidence of preordered or mesomorphic phase before polymer crystallization via shearing the polymer melt.

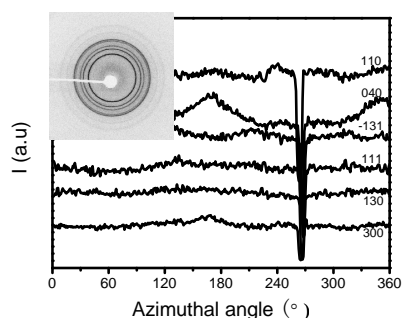


Figure 5. Azimuthal intensity curves of selected reflections after isothermal crystallization at 140 °C for iPP90 with shear rate 10 s^{-1} (The insertion is 2D WAXD patterns).

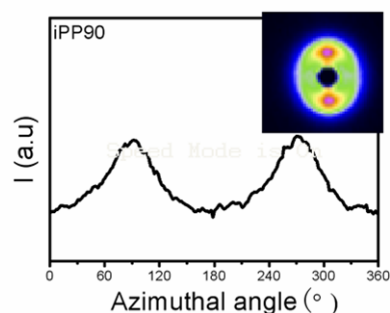


Figure 6. Azimuthal intensity curves of selected reflections after isothermal crystallization at 140 °C for iPP90 with shear rate 10 s^{-1} (The insertion is 2D WAXD patterns).

Figure 5 shows the blend iPP90 2D WAXD patterns and corresponding azimuthal intensity curves under the condition of shear-induced crystallization. Six diffraction rings are corresponding to 110, 040, -131, 111, 130 and 300 reflections. From the detailed

azimuthal intensity distributions of the reflections, one can see that under shear 10 s^{-1} , the crystallite reflections don't show obvious orientation except that the 040 reflection behaves some differently. Compared to weak degree of crystallite orientation under shear, lamellae is somehow much influenced. Figure 6 shows SAXS patterns of sample iPP90 after isothermal crystallization with shear rate 10 s^{-1} . When the blend crystallizes under the quiescent conditions, the scattering ring is isotropic. The scattering ring of sheared samples is anisotropic and the orientation happens. Most of oriented lamellae align perpendicular to the shear direction. The orientation exponent f introduced by Hermans is a used to investigate the degree of lamellar orientation[12] and the final value is 41%. In this work we find that shear can strongly influence the micro- and macrostructures of blend. Shear can bring orientation of both crystallite and lamellae structure especially it is obvious for lamellar orientation. The transient mesophase structure which is composed of folded chains is supposed to exist during the initial crystallization process even before shear composed. Under shear, many polymer chains go through coil-stretch transition and align parallel to the shear direction which induces the formation of oriented intermediate phase. The orientation structure will be retained with the competition between the orientation and relaxation of polymer chains with the annealing time. The strong lamellar orientation is attributed to a large amount of orientated mesomorphic phase in our experiment. The effect of shear on crystallite structure is much less which is attribute to its less observation scale than mesomorphic structure, thereby, the orientational degree correspondingly weakens. On all accounts we have reason to believe that there exists mesophase structure during the initial crystallization stage before shear composed.

References

- [1] F. J. Padden, H. D. Keith, "Spherulitic crystallization in polypropylene," *J. Appl. Phys.*, vol. 30, pp1479-1484, 1959.
- [2] D. R. Norton, A. Keller, "The spherulitic and lamellar morphology of melt-crystallized isotactic polypropylene," *Polymer*, vol. 26, pp704-716, 1985.
- [3] J. Karger-Kocsis, *Polypropylene: structure, blends and composites*, vol. 2. London: Chapman & Hall, 1995, pp.88-103.
- [4] H.G. Karian, *Handbook of polypropylene and polypropylene composites*. New York: Marcel Dekker Inc, 1999.
- [5] N. Kukaleva, M. Jollands, F. Cser, E. Kosior. "Influence of phase structure on impact toughening of isotactic polypropylene by metallocene-catalyzed linear low-density polyethylene," *J. Appl. Polym. Sci.*, vol. 76, pp1011-1018, 2000.
- [6] T. McNally, P. McShane, G.M. Nally, W.R. Murphy, M. Cook, A. Miller, "Rheology, phase morphology, mechanical, impact and thermal properties of polypropylene/metallocene catalysed ethylene 1-octene copolymer blends," *Polymer*, vol. 43, pp3785-3793, 2002.

- [7] K. Premphet, W. Paecharoenchai, "Polypropylene/metallocene ethylene-octene copolymer blends with a bimodal particle size distribution: Mechanical properties and their controlling factors," *J. Appl. Polym. Sci.*, vol. 85, pp2412-2418, 2002.
- [8] O. Prieto, J.M. Perena, R. Benavente, M.L. Cerrada, "Effect of composition and molecular weight on the crystallization behavior of blends of iPP and a metallocenic ethylene/1-octene copolymer," *Macromol. Chem. Phys.*, vol. 203, pp1844-1851, 2002.
- [9] P.D. Olmsted, W.C.K. Poon, T.C.B. Mcleish, N.J. Terrill, A. Ryan, "Spinodal-Assisted Crystallization in Polymer Melts," *J. Phys. Rev. Lett.*, vol. 81, pp373-376, 1998.
- [10] G. Strobl, "A thermodynamic multiphase scheme treating polymer crystallization and melting," *Eur. Phys. J. E*, vol. 18, pp295-309, 2005.
- [11] G. Strobl, "Crystallization and melting of bulk polymers: New observations, conclusions and a thermodynamic scheme," *Prog. Polym. Sci.*, vol. 31, pp398-442, 2006.
- [12] J.J. Hermans, P.H. Hermans, D. Vermeas, A. Weidinger, "Quantitative Evaluation of Orientation in Cellulose Fibers from X-Ray Fiber Diagrams," *Rec. Chim. Trav.*, vol. 65, pp427-447, 1946.